

# Pressure-induced unconventional superconductivity in topological insulator $\text{Bi}_2\text{Se}_3$

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Simultaneous low-temperature electrical resistivity and Hall effect measurements were performed on single-crystalline  $\text{Bi}_2\text{Se}_3$  under applied pressures up to 50 GPa. As a function of pressure, superconductivity is observed to onset above 11 GPa with a transition temperature  $T_c$  and upper critical field  $H_{c2}$  that both increase with pressure up to 30 GPa, where they reach maximum values of 7 K and 4 T, respectively. Upon further pressure increase,  $T_c$  remains anomalously constant up to the highest achieved pressure. Conversely, the carrier concentration increases continuously with pressure, including a tenfold increase over the pressure range where  $T_c$  remains constant. Together with a quasi-linear temperature dependence of  $H_{c2}$  that exceeds the orbital and Pauli limits, the anomalously stagnant pressure dependence of  $T_c$  points to an unconventional pressure-induced pairing state in  $\text{Bi}_2\text{Se}_3$  that is unique among the superconducting topological insulators.

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The interplay between superconductivity and topological insulator (TI) surface states has recently received enormous attention due to the observation of the long sought Majorana quasiparticle in InSb nanowires [1] and the promise of realizing topologically protected quantum computation [2]. Characterized by a non-trivial Z2 band topology with a bulk insulating energy gap that leads to a chiral metallic surface state with spin-momentum locking, TI surface states are analogous to the Quantum Hall edge state and arise at the surface of a TI material due to the topological nature of the crossover between a non-trivial bulk insulating gap and the trivial insulating gap of the vacuum [3]. The use of the proximity effect [4–7] to induce superconductivity in  $\text{Bi}_2\text{Se}_3$ , the most well studied TI material to date, has had success in coupling these two states but suffers from the presence of bulk conducting states which require gating to realize true TI supercurrents [8].

Theoretically, non-trivial surface Andreev bound states can be directly realized by opening a superconducting energy gap in a bulk conductor [9], which is why the quest for the topological superconductor is one of the most active areas in condensed matter physics. Recently, superconductivity has been found in materials with topologically nontrivial band structures, such as in  $\text{Cu}_x\text{Bi}_2\text{Se}_3$  [10–13] and  $\text{YPtBi}$  [14, 15], providing not only intrinsic systems with which to study the interplay between superconductivity and TI states, but also the potential to realize a new class of odd-parity, unconventional superconductivity [9].

The application of pressure has also uncovered superconductivity in several related materials, such as elemental Bi [16],  $\text{Bi}_2\text{Te}_3$  [17], and  $\text{Bi}_4\text{Te}_3$  [18], offering another route to realizing topological superconductivity. In this

study we measure transport properties of  $\text{Bi}_2\text{Se}_3$  over an extended pressure range to investigate the ground state at ultra-high pressures by using a designer diamond anvil cell capable of measuring both longitudinal and transverse resistivities up to 50 GPa. We observe the onset of a superconducting phase above 11 GPa that achieves a maximum transition temperature  $T_c = 7$  K above 30 GPa that maintains its value up to the highest pressures achieved in this study. We discuss the implications of an anomalously constant  $T_c$  that does not change with pressure, as well as an upper critical field that surpasses both orbital and Pauli limits, in terms of an unconventional superconducting state.

High quality single crystals of  $\text{Bi}_2\text{Se}_3$  were grown in excess selenium using the modified Bridgman technique described in detail elsewhere [19]. Single-crystal samples with approximate thickness 10  $\mu\text{m}$  and measured carrier concentration  $\sim 10^{17} \text{ cm}^{-3}$  were placed in contact with the electrical microprobes of an eight-probe designer designer diamond anvil cell [20] configured to allow combinations of both longitudinal and transverse four-wire resistance measurements. Pressures were determined from the shift of the ruby fluorescence line [21]. Electronic transport measurements were performed at pressures between 4.1 and 50.1 GPa using the standard 4-probe technique in both a dilution refrigerator and a pumped  $^4\text{He}$  cryostat, in magnetic fields up to 15 T directed parallel to the  $c$ -axis of the unpressurized ( $R\bar{3}m$ ) crystal structure of  $\text{Bi}_2\text{Se}_3$ .

Fig. 1 presents a summary of the longitudinal ( $\rho_{xx}$ ) resistivities as a function of both temperature and magnetic field measured at pressures above 13 GPa. (Resistivity data measured at lower pressures is presented elsewhere [22].) As shown previously, the evolution of both the tem-

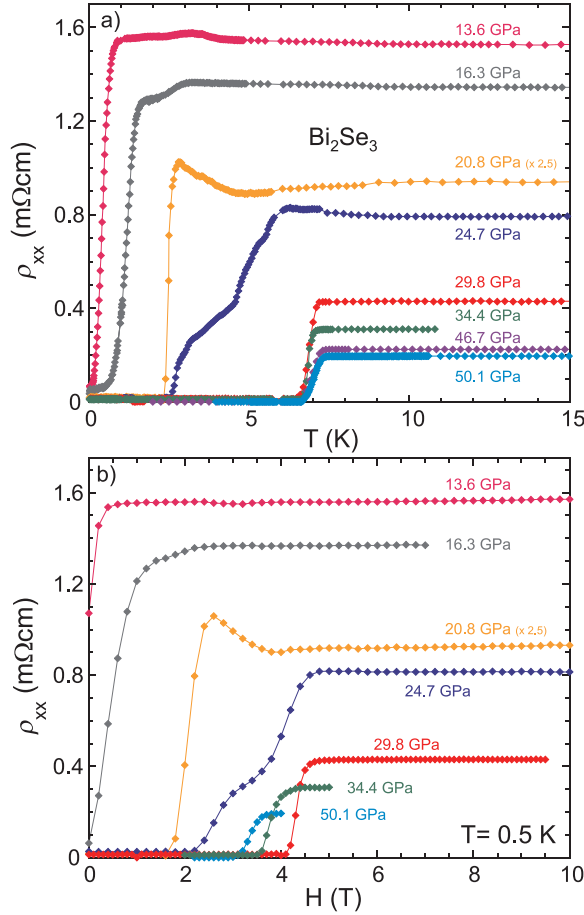


FIG. 1: Longitudinal resistivity of  $\text{Bi}_2\text{Se}_3$  for various applied pressures as a function of a) temperature and b) magnetic field oriented parallel to the crystallographic  $c$ -axis of the ambient pressure phase, at a fixed temperature of 0.5 K. (Data at 20.8 GPa were obtained with a different lead configuration resulting in larger measurement uncertainty, and are therefore scaled by a factor of 2.5 to match the overall trend reported previously [22].)

perature dependence and absolute values of  $\rho_{xx}$  indicates a metallization of the material with increasing applied pressure, in particular above 8 GPa where  $\rho_{xx}(300\text{ K})$  drops abruptly by an order of magnitude [22]. Just above this pressure, traces of superconductivity appear in the form of partial resistive transitions onsetting below 300 mK at 11.9 GPa (not shown) and gradually growing with increasing pressure. Interestingly, the value of carrier density where superconductivity first appears ( $\sim 10^{20}\text{ cm}^{-3}$ ) is close to the carrier concentration where superconductivity is seen in  $\text{Cu}_x\text{Bi}_2\text{Se}_3$  which may indicate that increased carrier concentrations are necessary for superconductivity in  $\text{Bi}_2\text{Se}_3$  [12]. As shown in Fig. 1a), a full resistive transition appears at 13.6 GPa with mid-point transition  $T_c = 0.5\text{ K}$  that gradually increases with increasing pressures up to  $\sim 30\text{ GPa}$ . Likewise, as presented in Fig. 1b), the upper critical field  $H_{c2}$  also grows

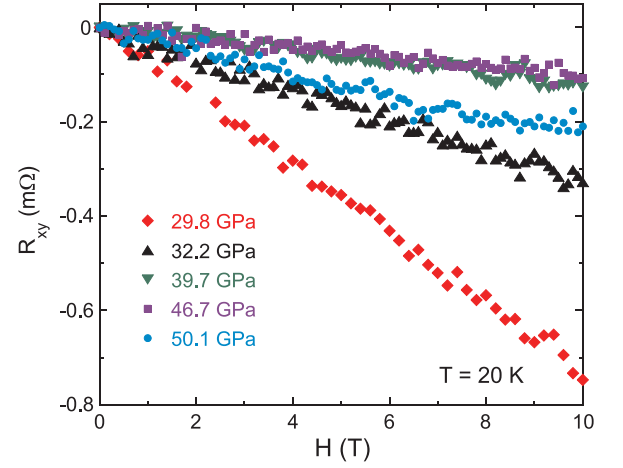


FIG. 2: Transverse Hall resistance of  $\text{Bi}_2\text{Se}_3$  as a function of applied pressure, showing negative and linear behavior with a slope that decreases with increasing pressure, indicative of a single electron-like band and a rapidly increasing carrier concentration (see text for details).

with pressure, with a magnetic field dependence very similar in form to the temperature dependence presented in Fig. 1a). Also, similar to the pressure evolution of  $T_c$ ,  $H_{c2}$  increases monotonically up to 30 GPa, above which both quantities abruptly stop growing and  $T_c$  remains strikingly constant at 7 K up to 50.1 GPa.

A transition temperature that is constant over such a large pressure range is highly anomalous. In conventional phonon-mediated superconductors like elemental Bi [16] and the two-band superconductor  $\text{MgB}_2$  [23],  $T_c$  typically decreases with increasing pressure due to phonon stiffening. However when the electronic bandwidth is sensitive to volume change, such as in transition metals, an increase in  $T_c$  with pressure is also possible [24]. This suggests that a balance between lattice dynamics and electronics is theoretically possible, as given by the expected dependence of  $T_c$  on both the phonon cutoff energy  $\Theta_D$  and the electronic density of states at the Fermi energy  $N(0)$ , as described by the BCS relation  $T_c \approx \Theta_D e^{-1/N(0)V}$ , with pairing potential  $V$  [25]. Such a case may be found in elemental Th, for which  $T_c$  begins to plateau with increasing pressure above  $\sim 8\text{ GPa}$  [26].

As shown in Fig. 2, a strong sensitivity of the transverse Hall resistance  $R_{xy}$  to pressure suggests that the electronic structure of  $\text{Bi}_2\text{Se}_3$  indeed undergoes a dramatic change with pressure. A one-band Drude approximation, motivated by the linear field dependence of  $R_{xy}$ , yields an estimated electron carrier density  $n_H$  that increases strongly with increasing pressure, consistent with the increasing metallicity observed in  $\rho_{xx}$ . As summarized in Fig. 3, this carrier density increases by over four orders of magnitude over the entire pressure range, suggesting significant changes in the band structure. More surprisingly,  $n_H$  increases by a factor of ten between 30 and

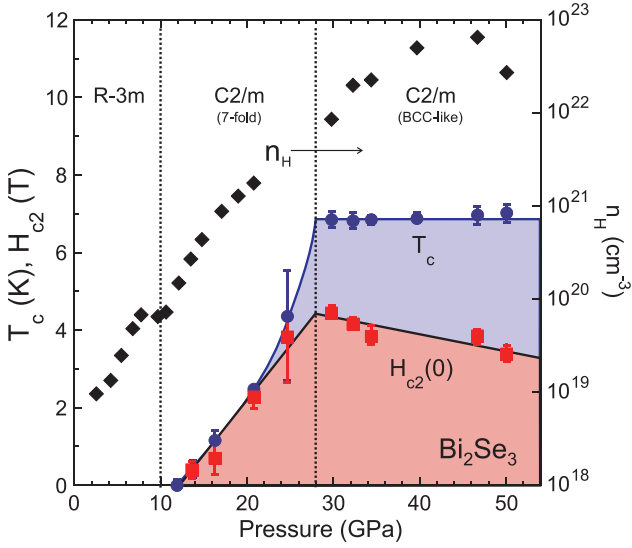


FIG. 3: Phase diagram of  $\text{Bi}_2\text{Se}_3$  showing the evolution of carrier concentration  $n_H$  (diamonds), superconducting transition temperature  $T_c$  (circles) and upper critical field  $H_{c2}$  at zero temperature (squares) as a function of pressure, for fields orientation along the crystallographic  $c$ -axis of the unpressurized structure. Dotted vertical lines correspond to known structural phase transitions between rhombohedral ( $R\bar{3}m$ ) and monoclinic ( $C2/m$ ) structures near 10 GPa, and a transition to a BCC-like ( $C2/m$ ) structure near 28 GPa, respectively [22, 27, 29].

50 GPa, the same range over which  $T_c$  remains constant. Given the exponential dependence of  $T_c$  on  $N(E_F)$ , such a contrast is very difficult to reconcile with standard BCS theory, with an exact balance between the two competing variables being highly unlikely due to the logarithmic sensitivity of both terms to pressure [23].

Moreover, the arrested evolution of  $T_c$  in  $\text{Bi}_2\text{Se}_3$  is in contrast to that observed in two other closely related compounds where  $T_c$  is strongly suppressed with pressure, as found in  $\text{Bi}_4\text{Te}_3$  [18] and the closely related TI material  $\text{Bi}_2\text{Te}_3$  [17]. Interestingly,  $\text{Bi}_2\text{Se}_3$  is known to undergo at least two structural transitions under pressure, from the ambient-pressure rhombohedral ( $R\bar{3}m$ ) structure to a lower-symmetry monoclinic ( $C2/m$ ) structure near 10 GPa, and then to an unknown phase above 28 GPa as measured by Raman spectroscopy [27]. In both  $\text{Bi}_2\text{Te}_3$  and  $\text{Bi}_4\text{Te}_3$ , superconductivity appears in the monoclinic phase and abruptly strengthens upon crossing a second structural transition into a cubic phase at higher pressures [18, 27, 28, 30–32]. Our preliminary x-ray diffraction experiments on  $\text{Bi}_2\text{Se}_3$  yield similar results, including a structural transition to a 7-fold ( $C2/m$ ) structure near 10 GPa followed by another transition to a BCC-like ( $C2/m$ ) structure above 28 GPa [29]. As shown in Fig. 3, the onset of superconductivity in  $\text{Bi}_2\text{Se}_3$  and its sharp increase to 7 K both coincide with these structural transitions in a manner similar to the other sys-

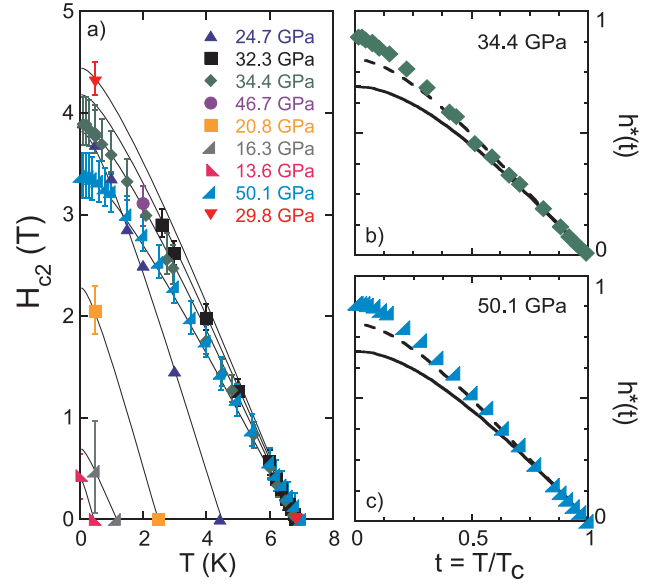


FIG. 4: (a) Upper critical field  $H_{c2}$  of  $\text{Bi}_2\text{Se}_3$  for various pressures up to 50 GPa, with fields applied parallel to the ambient-pressure crystallographic  $c$ -axis. Solid lines are guides, but all have the same functional dependence as  $H_{c2}(T)$  for 34.4 GPa data. Error bars for 24.7 GPa (not shown for clarity) are  $\pm 1$  T. Panels b) and c) present the reduced upper critical field,  $h^*(t)$  with reduced temperature  $t = T/T_c$ , for applied pressures of 34.4 and 50.1 GPa, respectively. Solid and dashed lines indicate the calculated  $h^*(t)$  dependence for orbital limited  $s$ -wave superconductors [33] and for a polar  $p$ -wave state [35, 36], respectively (see text).

tems, suggesting a close correlation among all of these high-pressure phases. However, with  $\text{Bi}_2\text{Te}_3$  and  $\text{Bi}_4\text{Te}_3$  both exhibiting a very notable rate of  $T_c$  suppression of  $\sim -0.13$  K/GPa after reaching their maximum values, it is clear that the behavior in  $\text{Bi}_2\text{Se}_3$  is anomalous.

The unique pressure evolution of  $T_c$  in  $\text{Bi}_2\text{Se}_3$  suggests the presence of a very unconventional superconducting state. This is further evidenced by an anomalous temperature dependence of the upper critical field  $H_{c2}(T)$ . To compare the data to known models, it is useful to calculate the reduced critical field,  $h^*(T) = \frac{H_{c2}(T)}{T_c} / \frac{dH_{c2}(T)}{dT}|_{T=T_c}$ , and compare it to models for orbitally limited  $s$ -wave [33] and spin-triplet  $p$ -wave [35, 36] superconductors. As shown in Figs. 4b) and c) for 34.4 and 50.1 GPa, respectively,  $h^*(T)$  deviates significantly from the expected orbital-limited behavior predicted by the Werthamer-Helfand-Hohenberg (WHH) theory for an  $s$ -wave superconductor,  $H_{c2}^{orb} \simeq 0.7T_c \times dH_{c2}/dT|_{T=T_c}$  (or  $h^*(0) \simeq 0.7$ ) [33]. This is true through the entire pressure range under study, and is immediately apparent in the observed near-linear temperature dependences of  $H_{c2}$  shown in Fig. 4a). Rather, the quasi-linear  $h^*(T)$  curves in Fig. 4 are closer in form to that of a  $p$ -wave superconductor as was suggested in the case of the unconventional heavy-fermion superconductor  $\text{UBe}_{13}$  [34],

although the measured  $h^*(0)$  values in  $\text{Bi}_2\text{Se}_3$  still slightly exceed the maximum value of  $h^*(0) \simeq 0.8$  expected for a polar  $p$ -wave state [35, 36].

To determine the influence of Pauli limiting, we calculate  $H_{c2}$  assuming that both orbital and paramagnetic pair breaking mechanisms are active. The Pauli limiting field  $H_P$  is determined by the Zeeman energy required to break Cooper pairs and equates to the gap energy  $\Delta$  (e.g.,  $H_P = 1.84T_c$  for a BCS superconductor) [37]. In the presence of both orbital and Pauli limiting, the expected upper critical field is modified to  $H_{c2}^\alpha = H_{c2}^{orb}/\sqrt{1+\alpha^2}$ , and determined by the Maki parameter  $\alpha \equiv \sqrt{2}H_{c2}^{orb}/H_P$  [38]. At 34.4 GPa, the calculated values  $H_{c2}^{orb} = 3.15$  T and  $H_P = 12.9$  T yield  $\alpha = 0.346$  and an expected modified value  $H_{c2}^\alpha = 2.80$  T, notably lower than the measured value of 4 T and indicative of an absence of Pauli pair-breaking. A similar case was presented for  $H_{c2}$  measurements of the related superconductors  $\text{Cu}_x\text{Bi}_2\text{Se}_3$  [39] and  $\text{YPtBi}$  [14, 40], which also both exhibit quasi-linear  $H_{c2}(T)$  behavior with zero-temperature values exceeding these universal limits. In addition,  $\text{Bi}_4\text{Te}_3$  under pressure also exhibits a linear  $H_{c2}(T)$  [18], presenting an intriguing set of strong spin-orbit-coupled superconducting materials with very similar anomalous features.

While exceeding the WHH limit can be considered a sign of unconventional superconductivity [36, 37] and can be explained by spin-triplet pairing, other mechanisms should also be considered. For instance, Fermi surface topology can enhance the expected WHH limit [41] as shown in the case of the pyrochlore superconductor  $\text{KOs}_2\text{O}_6$  [42], although such effects cannot arise from ellipticity alone [48]. Strong electron-phonon coupling can also slightly enhance the orbital limit [43, 44], although an excessive coupling constant of  $\lambda \simeq 4$  would be required to explain the observed  $h^*(0) \simeq 0.9$ . Strong spin-orbit scattering was shown early on to greatly reduce the effects of Pauli paramagnetic pair breaking [33], although a dramatic enhancement is only expected in the limit of infinite scattering strength. Finally, multi-band superconductivity can also instill deviations from WHH, as shown for  $\text{Lu}_2\text{Fe}_3\text{Si}_5$  [45], and calculated for  $\text{MgB}_2$  [46] and elemental Bi under pressure [47]. While such a case cannot be ruled out for  $\text{Bi}_2\text{Se}_3$ , the lack of evidence for multi-band behavior in the normal state transport suggests otherwise.

An anomalously large upper critical field that exceeds orbital and Pauli limits and a surprising insensitivity of  $T_c$  to pressure point to a very unique and unconventional superconducting state in  $\text{Bi}_2\text{Se}_3$ . The possibility of this state being topological in nature is an enticing consideration, but requires several as-yet unknown criteria to be satisfied. For instance, if band inversion symmetry is present, as well as a Fermi surface that is centered at time-reversal-invariant momenta such that a Dirac-type Hamiltonian describes the band structure, topological superconductivity is indeed probable given a fully

gapped pairing symmetry that is odd under spatial inversion [9]. Determination of both crystallographic and electronic structures in the high-pressure phase [29] are required to understand the implications for the pairing state and its relation to the ambient pressure topological insulator state.

In conclusion, the metallization of  $\text{Bi}_2\text{Se}_3$  at high pressures stabilizes a superconducting ground state above 11 GPa that appears to be optimized after a second structural phase transition above 28 GPa. The resulting phase diagram exhibits many similarities to those of other pressure-induced superconducting systems with strong spin-orbit coupling, including the role of structural transitions and the presence of an upper critical field that greatly exceeds the universal predictions for orbital and Pauli pair-breaking. In contrast to other materials, the persistence of a constant transition temperature over 20 GPa of applied pressure in  $\text{Bi}_2\text{Se}_3$  presents a challenge to explanations involving phonon-mediated pairing, suggesting an unconventional superconducting state.

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